

AD-A233 881

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1. REPORT NUMBER (blank)	2. REPORT DATE 1989	3. REPORT TYPE AND DATES COVERED Proceedings Paper	
4. TITLE AND SUBTITLE The Effect of Annealing on the Thermal and Dynamic Mechanical Properties of TMXDI Based Polyurethanes *		5. FUNDING NUMBERS Work Unit #59-1472-0-9 Assession #DN280-003	
6. AUTHOR(S) G. M. Stack		8. PERFORMING ORGANIZATION REPORT NUMBER DTIC ELECTE APR 05 1991	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Elastomer Science Sec., Acoustic Materials Branch, Underwater Sound Reference Detachment Naval Research Laboratory PO Box 568337 Orlando, FL 32856-8337		9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research	
11. SUPPLEMENTARY NOTES*Paper appeared in Proceedings of the 18th North American Thermal Analysis Society Conference Volume II, 1989) pp 802-808		10. SPONSORING/MONITORING AGENCY REPORT NUMBER DTIC ELECTE APR 05 1991	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A series of polyurethane model compounds based on the meta and para isomers of tetramethyl xylene diisocyanate have been prepared. These urethanes contained soft segments based on polycaprolactone. The urethanes obtained from the para isomer contained crystalline hard segments as revealed by the presence of an endothermic peak in Differential Scanning Calorimetry experiments. A series of high temperature annealing studies were performed to determine the effect of thermal treatment on the melting behavior of these crystalline polyurethanes. It was found that annealing these urethanes at temperatures from 100 to 160 deg C resulted in an increase of up to 40 deg C in the position of the DSC endothermic peak. Subsequent low temperature DSC experiments indicated the annealing caused a small change in the urethane's soft segment glass transition temperature. This result indicates a change in the extent of phase separation may have occurred. Dynamic mechanical measurements were made on these annealed urethanes by means of a resonance method developed at our laboratory. These experiments indicate that high temperature annealing also affects the dynamic mechanical behavior of the polyurethane.			
14. SUBJECT TERMS Polyurethanes Tetramethyl xylene diisocyanate Differential scanning calorimetry		15. NUMBER OF PAGES 8	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT SAR			

NSN 7540-01-280-5500

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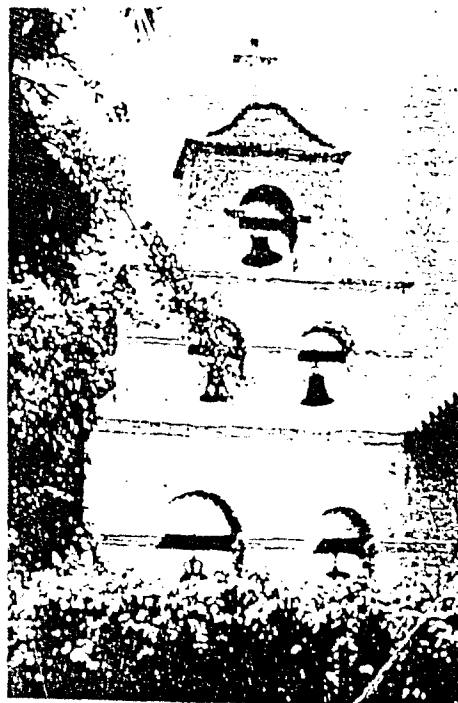
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Proceedings of the eighteenth
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THERMAL ANALYSIS
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VOLUME II



September 24-27, 1989
San Diego, California

The Effect of Annealing on the Thermal and Dynamic
Mechanical Properties of TMXDI based Polyurethanes

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A series of polyurethane model compounds based on the meta and para isomers of tetramethyl xylene diisocyanate have been prepared. These urethanes contained soft segments based on polycaprolactone. The urethanes obtained from the para isomer contained crystalline hard segments as revealed by the presence of an endothermic peak in Differential Scanning Calorimetry (DSC) experiments. A series of high temperature annealing studies were performed to determine the effect of thermal treatment on the melting behavior of these crystalline polyurethanes. It was found that annealing these urethanes at temperatures from 100 to 160°C resulted in an increase of up to 40°C in the position of the DSC endothermic peak. Subsequent low temperature DSC experiments indicated that the annealing caused a small change in the urethane's soft segment glass transition temperature. This result indicates that a change in the extent of phase separation may have occurred. Dynamic mechanical measurements were made on these annealed urethanes by means of a resonance method developed at our laboratory. These experiments indicate that high temperature annealing also affects the dynamic mechanical behavior of the polyurethane.

The Effect of Annealing on the Thermal and Dynamic
Mechanical Properties of TMDI Based Polyurethanes

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INTRODUCTION

Polyurethanes are promising candidates for a variety of underwater acoustic applications where specific dynamic mechanical properties are required. In order to design polyurethanes with specific acoustic properties it is necessary to obtain an understanding of the factors which affect the dynamic mechanical properties of a polyurethane elastomer. A series of polyurethane model compounds based on the meta and para isomers of the aliphatic isocyanate, tetramethyl xylene diisocyanate (TMDI), have been prepared. A systematic study of the effect of compositional parameters on the dynamic mechanical properties of these urethanes has been performed. In addition to changes in composition, the properties of polyurethanes can also be significantly affected by thermal treatment. This has been demonstrated in several polyurethanes systems other than those based on TMDI.²⁻⁴ In this paper, we report the results of a recent investigation where selected TMDI polyurethanes were subjected to high temperature annealing and their thermal and dynamic mechanical properties were then determined. These experiments were performed on the urethanes based on the para isomer of TMDI. The para based urethanes contained crystalline hard segments, which were identified by the presence of an endothermic peak in Differential Scanning Calorimetry (DSC) experiments.

EXPERIMENTAL

The polyurethane prepolymers were obtained from American

Cyanamid Company. These prepolymers were synthesized by reacting an excess of diisocyanate with the polyol as described previously.⁵ Prepolymers were made with differing amounts of excess isocyanate in order to obtain polyurethanes with varying hard segment contents. Polycaprolactone with a molecular weight of approximately 2000g/mole was used as the polyol. These prepolymers were cured into polyurethane elastomers using 1,4 butanediol and a small amount (0.01%-0.04%) of the metal catalyst, ferric acetylacetonate. The prepolymer and curative were heated to 70°C, degassed, mixed thoroughly, and poured into a preheated mold. The polyurethane was allowed to cure at 70°C for 24 hours, demolded, and postcured at ambient conditions for at least two weeks. Calorimetric measurements were made using a Perkin Elmer Differential Scanning Calorimeter, DSC4. The polyurethane melting endotherms were measured from 50 to 250°C using a heating rate of 20°C/min and sample masses in the range of 10 mg. Additional low temperature scans from -100 to 0°C were made using liquid nitrogen as a coolant. Annealings were performed directly in the DSC by heating at 10°C/min to a selected temperature and maintaining the sample at this temperature for a specific length of time. Larger samples suitable for dynamic mechanical analysis were annealed under vacuum in an oven which was preset to the selected temperature. Dynamic mechanical properties were measured by means of a resonance method developed at NRL-USRD.⁶ The sample is harmonically excited using discrete frequency excitation. By solving the equations of motion, the Young's modulus and loss tangent of the sample are obtained. The dynamic moduli are extrapolated to higher frequencies using a time-temperature superposition principle.

RESULTS AND DISCUSSION

High temperature DSC scans revealed the presence of a broad endothermic peak in the para TMDI based polyurethanes. The peak melting point and enthalpy of fusion were found to increase with increasing hard segment content, and the results are summarized in Table 1. The melting point and enthalpy of fusion of the 30% hard segment content polyurethane were further increased by dissolution into methylene chloride and recrystallization. Samples were annealed at selected temperatures for at least 18 hours. The effect of these thermal treatments on the position of the peak melting point was determined by subsequent heating of the annealed samples in the DSC. The results obtained for the urethane with 30% hard segment content is shown in Figure 1. Annealing at temperatures in the range from 100 to 160°C caused an increase

of over 40°C in the position of the endothermic peak. These thermal treatments were also found to affect the enthalpy of fusion of this endothermic peak. The resultant enthalpies of fusion for the polyurethane recrystallized from methylene chloride are plotted as a function of annealing temperature in Figure 2. The enthalpy of fusion is increased by increasing the annealing temperature. But at annealing temperatures higher than 140°C there was a significant decrease in the enthalpy. This decrease in enthalpy at the higher annealing temperatures is also observed in the other polyurethanes studied.

A low-temperature glass transition was observed in these urethanes, which may be attributed to the glass transition of the polycaprolactone soft segment. The effect of high temperature annealing on the position of this glass transition was also determined. It was found that a slight increase in the glass transition temperature occurred after these thermal treatments. An example of this effect is shown in Figure 3 for the polyurethane with 30% hard segment content. For this sample, the glass transition temperature increased steadily as a function of annealing temperature. The highest annealing temperature of 160°C caused an increase of over 3°C in the position of this glass transition temperature. An increase in the soft segment glass transition temperature of a polyurethane normally indicates that there is an increased amount of mixing between the hard and soft segment phases of the polyurethane.

These DSC results can be interpreted by considering that the annealings cause an increase in the crystallite size of the hard segments. This increase would be consistent with the observed increase in the temperature of the endothermic peak. It is likely that the smaller hard segments could not be accommodated in these larger hard segment crystallites and would dissolve into the soft segment. This analysis would explain the decreased enthalpy of fusion and increased soft segment glass transition temperature caused by the higher temperature annealings.

Dynamic mechanical measurements were made over a wide frequency range on some of the annealed polyurethanes by means of a resonance method. The dynamic Young's modulus of the polyurethane with 29% hard segment content is shown in Figure 4 both before and after high temperature annealing. It is clear that the annealing at the lower temperature of 110°C has little effect on the modulus of this urethane. However, the higher annealing temperature of 145°C is seen to cause a significant increase in the modulus of this urethane. The loss tangents for these samples are shown as a function of frequency in Figure 5. The increase in the loss tangent at

high frequencies in the unannealed sample is due to the onset of the glass transition of the polycaprolactone soft segment. In the annealed samples there is less increase of the loss tangent as a function of frequency and the value of the loss tangent at low frequencies is increased. These observations suggest that the soft segment glass transition has been broadened and shifted to higher temperatures by the annealings. This conclusion is consistent with the model of increased phase mixing in the annealed polyurethanes, which was deduced from the analysis of the DSC results.

CONCLUSIONS

High temperature annealing is found to raise the hard segment melting point and appears to increase the extent of phase mixing between the hard and soft segments. These changes cause an increase in the urethane's modulus and a broadening of its loss tangent peak.

ACKNOWLEDGMENTS

This work is supported by the Office of Naval Research.

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Table 1. The thermal properties of p-TXDI based polyurethanes.

HARD SEGMENT CONTENT (%)	METHOD OF PREPARATION	ENDOTHERMIC PEAK (°C)	ENTHALPY OF FUSION (cal/g)
23	AS CURED	132.3	1.65
29	AS CURED	149.1	2.7
30	AS CURED	150.8	2.3
30	RECRYSTALLIZED FROM CH ₂ Cl ₂	174.6	3.3

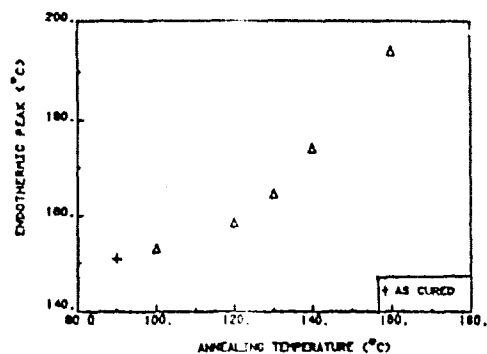


Figure 1. Plot of the endothermic peak temperature as a function of annealing temperature for a p-TMXDI based polyurethane.

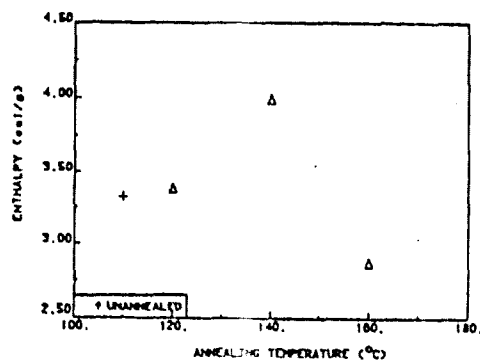


Figure 2. Plot of the enthalpy of fusion as a function of annealing temperature for a p-TMXDI polyurethane.

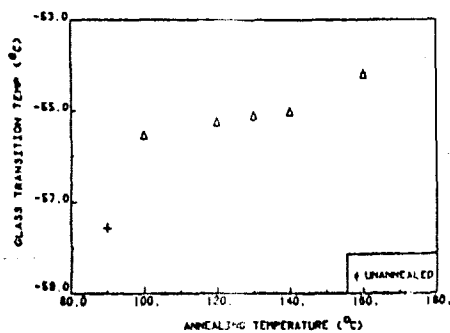


Figure 3. Plot of the soft segment glass transition temperature as a function of annealing temperature for a p-TMXDI urethane.

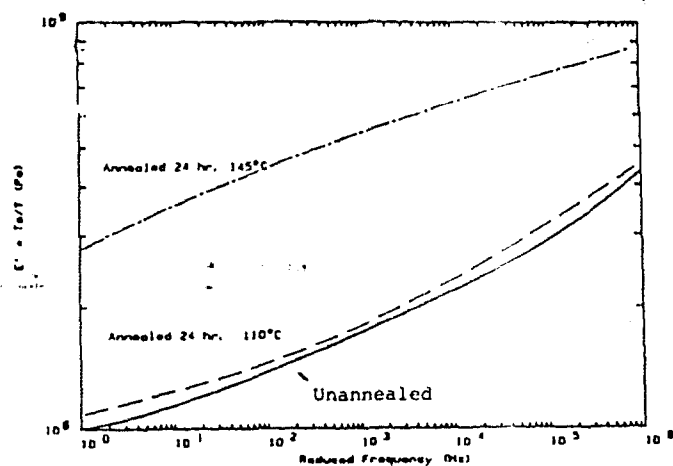


Figure 4. Plot of the dynamic Young's modulus as a function of frequency for a polyurethane after the indicated thermal treatments measured at 5°C.

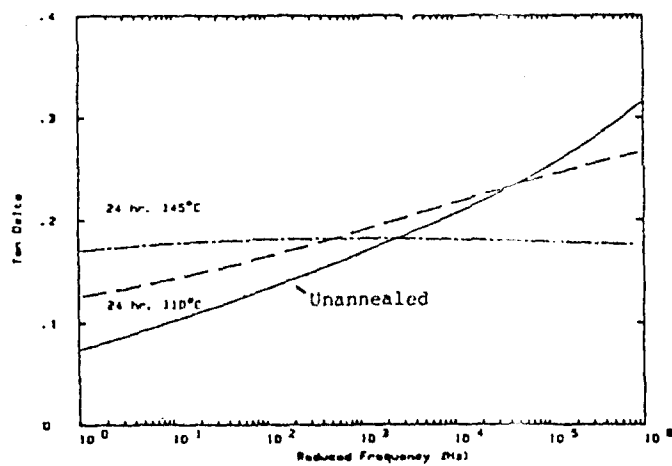


Figure 5. Plot of the loss tangent as a function of frequency for a polyurethane after the indicated thermal treatments measured at 5°C.